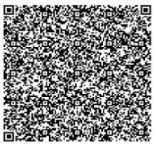

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An Introductory Note on the Spectrum and Energy of Molecular Graphs

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Abstract

Graph Theory is one branch of Mathematics that laid the foundations of the structural studies in Chemistry. The fact that every molecule or compound can be represented as a network of vertices (elements) and edges (bonds) provoked the question of the predictability of the physical and chemical properties of molecules and compounds. Spectrum, π-electron energy, Spectral Radius etc. are predictable using graph theoretical methods. This is an introductory paper about spectrum and energy of molecular graphs.

Keywords: Molecular Graph, Spectrum, Energy, Spectral Radius

1. Introduction

The fascinating world of graph theory goes back several centuries and revolves around the study of graphs- mathematical structures showing relations between objects. The origin of Graph Theory and Topology dates back to when the famous Swiss Mathematician Leonhard Euler (1707 - 1783) solved the *Konigsberg Bridge Problem* in 1736. Since then, the subject has grown both in its theory and its

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varied applications. The celebrated *4 Color Problem* which was a major unsolved problem since 1852 and its unique method of solution using computers in 1976 - the first of its kind in Mathematics, also belongs to Graph Theory. Graphs can be used to model many types of relations and processes in chemical, physical, biological, social and information systems.

The skeletal formula of a molecule is nothing but a graph. This means that any compound or molecule can be represented as a graph. However, many graphs do not have a corresponding molecule or compound. The molecular formula of methanol (methyl alcohol) is CH_3OH. The skeletal formula and the respective graph are given in Figure 1 and Figure 2, respectively.

Graphs can also represent compounds with doubled bonds by parallel edges. The Kekulé structures of benzene and the corresponding graphs are given in Figure 3 and Figure 4.

In the 1930's Erich Hückel [2] proposed the famous **Hückel Molecular Orbital Theory (HMO)**. The conjugated hydrocarbon can be represented by a graph called molecular graph according to the rule: every carbon atom is represented by a vertex and every carbon-carbon bond by an edge, hydrogen atoms are ignored. The eigenvalues of the molecular graph represent the energy level of the electron in a molecule. In HMO approximation, the energy of the ith molecular orbital is given by $E_i = \alpha + \lambda_i \beta$, where α and β are constants (The method assumes that the Hamiltonian operator is a simple linear combination of certain orbitals, and uses the time-independent Schrodinger equation to solve for the energies desired).

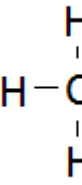

Figure 1

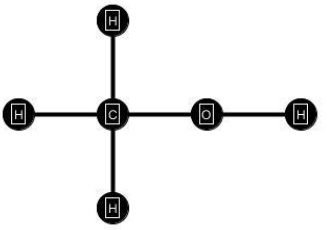

Figure 2

The total π-electron energy (E) is equal to the sum of the energies of all π-electrons that are present in the respective molecule, -i.e., $E = \sum_{i=1}^{n} g_i E_i \sum_{i=1}^{n} g_i \lambda_i$, where g_i is the number of electrons in the ith molecular orbital (whose energy is E_i).

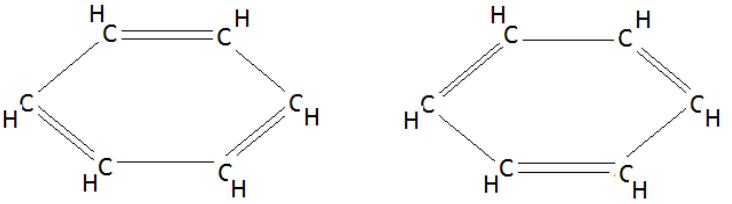

Figure 3

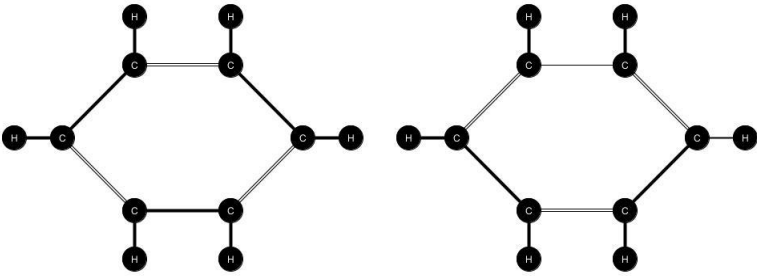

Figure 4

2. Spectral Graph Theory

Spectral graph theory is a study of the relationship between the topological properties of a graph with the spectral (algebraic) properties of the matrices associated with the graph. Originally, spectral graph theory analyzed the adjacency matrix of a graph, especially its eigenvalues. One of the main motivations behind spectral graph theory is to establish connections of the graph's intrinsic structures, such as connectivity, diameters, embeddability, chromatic numbers, with the spectra of various associated matrices, such as the adjacency matrix, the incidence matrix, and the Laplacian matrix, to name a few.

The spectral theory of graphs emerged as an active research frontier in graph theory since the 1950s. Collatz and Sinogowitz first began the exploration of this topic in 1957.[29] It has since then had a major impact on combinatorics, computer science, operations research, biology, and social science.

In spectral graph theory, let G be a finite undirected simple graph with vertex set V(G) and edge set E(G). The **order** of G is the number of vertices in G. A graph of order n is also called an n-vertex graph. The **size** of G is the number of edges in G. Let G(n,m) denote an arbitrary graph of order n and size m. The **adjacency matrix** A(G) of the graph G is a square matrix of order n, whose (i, j)-entry is equal to 1 if the vertices v_i and v_j are adjacent and equal to zero otherwise. The characteristic polynomial of the adjacency matrix, i.e., det(λI_n –A(G)), where I_n is the unit matrix of order n, is said to be the **characteristic polynomial of the graph** G and will be denoted by φ(G, λ).

From linear algebra it is known that the graph **eigenvalues** $\lambda_1, \lambda_2, \ldots, \lambda_n$ are the solutions of the equation $\varphi(G,\lambda) = 0$. The eigenvalues of the adjacency matrix A(G) form the **spectrum,** spec(G), of the graph. If the distinct eigenvalues of G are $\lambda_1, \lambda_2, \ldots, \lambda_m$ with multiplicities $t_1, t_2 \ldots t_m$ respectively, then, spec(G) is written as $\begin{pmatrix} \lambda_1 & \lambda_2 & \ldots & \lambda_m \\ t_1 & t_2 & \ldots & t_m \end{pmatrix}$ or ${\lambda_1}^{t_1}, {\lambda_2}^{t_2}, \ldots, {\lambda_m}^{t_m}$. The sum of all eigenvalues, being the trace of the adjacency matrix is zero. The largest eigenvalue of a graph is also known as its **spectral radius**. Since A is real and symmetric, all its eigenvalues are real. Multiplicity of λ as a root of the equation det (A- λ I_n) =0 is equal to the dimension of the space of the eigenvectors corresponding to λ.

Generalization of the formula valid for the total π-electron energy of a conjugated hydrocarbon calculated by the HMO method was given by Ivan Gutman [2] in the late 1970s who defined the **energy E(G) of a graph G** as the sum of the absolute values of its eigenvalues. Gutman conjectured that among all graphs of order n, the complete graph K_n has maximum energy. H. B. Walikar disproved Gutman's conjecture and produced graphs whose energy exceed that of K_n and called such graphs as hyperenergetic. We call an n-vertex graph G **hypoenergetic** if E(G) < n and

hyperenergetic if E(G) > 2(n – 1). The first systematic construction of hyperenergetic graphs was proposed by Walikar, Ramane, and Hampiholi [2], who showed that the line graphs of K_n , n ≥ 5, and of $K_{n/2,n/2}$, n ≥ 8, are hyperenergetic. Two nonisomorphic graphs are said to be **equienergetic** if they have the same energy. If the spectra of two graphs are identical, then the graphs are said to be **cospectral**. It has been proved [4] that if the energy of a graph is rational then it must be an even integer. If G is a k-regular graph on n vertices, R. Balakrishnan [3] proved $E(G) \leq k + \sqrt{k(n-1)(n-k)} = B_2$, a sharp bound. He also proved that for each $\in > 0$, there exist infinitely many n for each of which there exists a k-regular graph G of order n with $k < n - 1$ and $E(G)/B_2 < \in$. **Energy of cluster and bipartite cluster** graphs [26, 27] have been determined by H. B. Walikar and H. S. Ramane, where a cluster graph has large number of edges.

3. Spectrum, Energy and Spectral Radius of Some Graphs

The spectrum, energy, spectral radius of some class of graphs are listed below:

- The eigenvalue of an empty graph is zero. [2]
- The spectral radius of a k-regular graph (all vertices have degree k) is k. [2]
- If G is a connected graph, then the spectral radius is less than or equal to the largest degree of the graph. [29]
- The adjacency matrix of a bipartite graph has the form $A = \begin{bmatrix} 0 & B \\ B^T & 0 \end{bmatrix}$. It follows that the spectrum of a bipartite graph is symmetric w.r.t. 0: if [u v] is an eigenvector with eigenvalue θ, then [u -v] is an eigenvector with eigenvalue − θ. [1]
- The spectrum of complete graph K_n on n vertices is $(n-1)^1$, $(-1)^{n-1}$ and energy is equal to 2(n – 1). [1]
- The spectrum of complete bipartite graph $K_{m,n}$ is 0^1, m^{n-1}, n^{m-1}, $(m+n)^1$. [1]

- The energy of the complete bipartite graph $K_{n-1,1}$, also known as the star [2] is $2\sqrt{n-1}$. [2]
- The spectrum of the n- cycle is $2\cos(2\pi j/n)$ ($j = 0, \ldots, n-1$). [1]
- The spectrum of the path P_n on n vertices is $2\cos(\pi j/(n+1))$ ($j = 1, \ldots, n$). [1]

4. Method to compute graph energy

A classical result of the theory of graph energy [2] is that E(G) can be computed from the characteristic polynomial of G by means of **Coulson Integral Formula**,

$$E(G) = \frac{1}{\pi}\int_{-\infty}^{\infty}\left[n - \frac{ix\varphi'(G,ix)}{\varphi(G,ix)}\right] dx,$$

where φ'(G, λ) denotes the first derivative of φ(G, λ).

5. Different Graph Energies

There have been several recent attempts to extend the graph-energy concept to eigenvalues of matrices other than the adjacency matrix. Especially much work has been done on the so-called **Laplacian graph energy** based on the spectrum of the Laplacian matrix. The Laplacian is an alternative to the adjacency matrix for describing the adjacent vertices of a graph. The Laplacian, L, of a graph is the square matrix that corresponds to the vertices of a graph. The Laplacian can be derived from D – A, where D is the diagonal matrix whose entries represent the degrees of the vertices, and A is the adjacency matrix. The smallest eigenvalue of L is 0. The multiplicity of 0 as an eigenvalue of L is the number of connected components in the graph. The Laplace spectrum of a finite undirected graph without loops is the spectrum of the Laplace matrix L. Since L is real and symmetric, the Laplace spectrum is real.

A concept called **distance energy** [21] of graphs was introduced by Gopalapillai Indulal, Ivan Gutman and Ambat Vijayakumar. The **distance matrix** D = D(G) of G is defined so that its (i, j)-entry is

equal to $d_G(v_i, v_j)$, the distance (= length of the shortest path) between the vertices v_i and v_j of G. The D-eigenvalues of a graph G are the eigenvalues of its distance matrix D, and form the D-spectrum of G. The D-energy $E_D(G)$ of the graph G is the sum of the absolute values of its D-eigenvalues. Two graphs are said to be D-equienergetic if they have equal D-energies. Bounds for the distance spectral radius [21] and Distance energy of graphs of diameter 2 were calculated. The D-spectrum of the cartesian product [22] of two distance regular graphs, lexicographic product G[H] of two graphs G and H when H is regular, Hamming graphs Ham(d; n) of diameter d and order n^d and those of the C_4 nanotori $T_{k,m,C4}$, of the join of regular graphs [23], of some self-complementary graphs [24], of the neighbourhood corona, G_1*G_2 [25] where G_1*G_2 is the graph obtained by taking n copies of graph G_2 and for each i , making all vertices in the ith copy of G_2 adjacent with the neighbours of v_i from the vertex set $\{v_1 , v_2 , \ldots, v_n\}$ of G_1 have been studied.

Yang et al. (1994) [28] defined the **extended adjacency matrix A_{ex} of G** whose (i , j)-entry is equal to $\frac{1}{2}\left(\frac{d_i}{d_j} + \frac{d_j}{d_i}\right)$ if the vertices v_i and v_j are adjacent, and 0 otherwise,. A very recent work was done by Kinkar Ch. Das, Ivan Gutman, Boris Furtula who examined the lower and upper bounds on spectral radius and the energy E_{ex} of the A_{ex} -matrix .

Apart from the above defined energies, depending on the matrix, the concept of color energy [5], minimum covering energy [6], reduced color energy [7, 8], minimum degree energy [9], maximum degree energy [10], minimum neighbourhood energy [11], common–neighborhood energy [12], non-common neighbourhood energy [13], labeled graph energy [14], minimum dominating seidel energy [15], maximum eccentricity energy [16] of a graph were introduced. Basic properties of the corresponding energy were studied and the bounds were determined. R. Khanna, B. N. Dharmendra and G. Sridhara [11] are the authors of the papers on minimum dominating distance energy, minimum dominating energy and Laplacian minimum dominating energy of a graph. C. Adiga , R. Balakrishnan, Wasin So showed [17] interest to study

about the energy of the skew-adjacency matrix of a directed graph D. C. Adiga and M. Smitha [18] studied the skew Laplacian energy of a simple, connected digraph. The minimal value of this energy in the class of all connected digraphs on $n \geq 2$ vertices was determined.

6. Construction of Equienergetic graphs

Pairs of equiregular distance equienergetic graphs of diameter 2, on $p = 3t + 1$ vertices were constructed. Pairs of connected, non cospectral, equienergetic graphs with equal number of vertices, equal number of edges have been constructed by H. S. Ramane et al [19]. Again, H. S. Ramane et al. [20] constructed pairs of connected, noncospectral, equienergetic graphs of order n for all $n \geq 9$. Two non cospectral equienergetic graphs [3] of order 4n, where n is a positive integer ≥ 3 have been constructed.

7. Applications

Spectral Graph theory is an important multidisciplinary area of science that uses the methods of Linear Algebra to solve problems in Graph Theory and, on the other hand, it has been used to model and treat problems in Chemistry, Computer Science, Physics, Operational Research, Combinatorial Optimization, Biology, Bioinformatics, Geography, Economics and Social Science, among others. Spectral graph theory is used in the study of DNA. A molecule of DNA is a very long string consisting of a unique sequence using four amino acids. The goal is to determine this sequence for a given molecule of DNA. These methods employ spectral ordering involving the Laplacian and permuted matrices. Graph spectra appear in internet technologies, pattern recognition, computer vision and in many other areas. One of the oldest applications (from 1970's) of graph eigenvalues in Computer Science is related to graphs called expanders. The Laplacian eigenvalues determine the kinematic behavior of a liquid flowing through a system of communicating pipes. The basic behavior of the flow is determined by the second smallest Laplacian eigenvalue. The second largest eigenvalue of a graph gives

information about expansion and randomness properties. The smallest eigenvalue gives information about independence number and chromatic number. Interlacing gives information about substructures. The fact that eigenvalue multiplicities must be integral provides strong restrictions.

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